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Working Group on the State of the Environment and Nature
Conservation

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Document title	Determination of total alkalinity – proposed monitoring guidelines
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Submitted by	Sweden

Background

HELCOM guidelines for hydrography and hydrochemistry are currently being revised. Lead Country Sweden submits proposed guidelines for determination of total alkalinity in the HELCOM area as a contribution to the ongoing revision of HELCOM monitoring guidelines. Draft guidelines for alkalinity were discussed at STATE&CONSERVATION 4-2016 (para 2MA.20) that supported the proposal from Sweden to include the guidelines in the sub programme 'Water column chemical characteristics' of the HELCOM Monitoring Manual. The guidelines have been amended based on reviews by Co-lead country Poland, as well as representatives from Denmark, Estonia, Finland and Germany.

Measurements of alkalinity are currently described in Annex B-15 in *Manual for marine monitoring in the COMBINE program*. The new guidelines include updates on procedure, and stresses the importance of monitoring of alkalinity.

Action requested

The Meeting is invited to endorse the draft guidelines for determination of total alkalinity.

Determination of total alkalinity

1 Background

1.1 Introduction

Although not listed among HELCOM Core Indicators, alkalinity must be monitored to provide information of alterations in the carbonate buffer system which may be induced by changing weathering processes on the continents or internal processes in the Baltic Sea. Although alkalinity is not affected by increasing atmospheric CO₂, it controls the pH at a given atmospheric CO₂ level. Hence its long-term changes are interacting with ocean acidification induced by the dissolution of anthropogenic CO₂.

1.2 Purpose and aims

The aim of monitoring is to identify spatial variations and temporal trends in total alkalinity.

2 Monitoring methods

2.1 Monitoring features

Total alkalinity (A_T) is defined as amount of protons required to compensate the excess of proton acceptors over proton donors (hydrogen ions) 1 kg of seawater. For a full definition and an overview of contributing ion species, see Dickson (1981).

2.2 Time and area

Monitoring covers the entire Baltic area, and is performed throughout the whole year.

2.3 Monitoring procedure

2.3.1 Monitoring strategy

When studies of the carbonate buffer system are performed, four variables are considered: total alkalinity (A_T), pH, dissolved inorganic carbon (DIC) and partial pressure of carbon dioxide (pCO_2).

Theoretically, when two of these components are accurately determined, the remaining two can be calculated. These calculations, while valid for oceanic water, does not take into account contributions from dissolved organic material. The conditions in the Baltic Sea with relatively high levels of humic matter and other dissolved organic components are more complex (Kuliński *et al* 2014, Ulfsbo *et al* 2015). This results in calculated A_T values that are lower than those obtained from measurements. This has to be taken into account when determining the state of the marine CO₂ system based on AT measurements.

Alkalinity should be determined by potentiometric titration, with an appropriate endpoint determination.

2.3.2 Sampling method and equipment

Samples should be collected into gas-tight capped glass bottles (e. g. Pyrex bottles). Bottles should be rinsed with sample water before filling. Since alkalinity is not changed by the addition/removal of gaseous CO₂, either by gas exchange or biological activity, it is not necessary to avoid contact with ambient air. However, there is one exception: Ulfsbo *et al.* (Mar. Chem., 2011) reported that the monitoring alkalinity data for H₂S-containing waters which they used in their study, were biased due to the oxidation of H₂S by contact with ambient air. A head space of 1 % with respect to the total sample volume is already sufficient to oxidize approximately 50 μmol-H₂S/l. This has to be taken into account when determining the alkalinity in anoxic waters.

2.3.3 Sample handling and analysis

2.3.3.1 Sample handling

Since biological consumption/generation of CO₂ does not affect the alkalinity, it is not necessary to poison the samples before storage. Nevertheless, it is recommended to store the samples at low temperatures and darkness, and to analyze the samples within a few weeks in order to avoid any other (unknown) biogeochemical reactions that may affect the alkalinity.

2.3.3.2 Analytical procedure

A known amount of sample is titrated with a solution of hydrochloric acid until the equivalence point can be calculated. Titration procedure is monitored with a pH glass electrode. Titration is continued until a final pH of approximately 3.0. Calibration of the electrode is not necessary as long as IRM or CRM are analysed, but rinse the electrode and temperature probe with deionized water and wipe between calibrants/samples.

In a controlled laboratory environment, an analytical balance is used for determination of sample size. If the analytical procedure is performed on board a vessel during a sampling cruise, it is better to use a volumetric method. Density of the sample water is calculated from temperature and salinity.

Automated burettes are commercially available, as well as software for data collection and processing. Hydrochloric acid, 0.01 – 0.05M is used for the titration. The titer of the hydrochloric acid needs to be correctly determined; ampoules of hydrochloric acid with certified concentration are commercially available.

2.4 Data analysis

When density of seawater is used for calculations, equation of state of seawater (Millero and Poisson 1981) should be used.

3 Data reporting and storage

Data should be reported as $\mu\text{mol kg}^{-1}$. Data is reported annually to the HELCOM COMBINE database, hosted by ICES.

4 Quality control

4.1 Quality control of methods

Laboratories carrying out determination of total alkalinity should have established a quality management system according to EN ISO/IEC 17025.

Collect and analyze samples for estimation of measurement uncertainty (repeated measurements from a sample, multiple subsamples from different samplers closed at same depth).

Equipment used (analytical balance, pH electrode, thermometer probe) must be calibrated and their accuracy monitored.

Make sure emf value of electrode for each calibrant is within range recommended by manufacturer.

An internal reference material (IRM) should be analyzed daily.

A certified reference material (CRM) is provided by Scripps Institute of Oceanography of the University of California, San Diego.

4.2 Quality control of data and reporting

Measurement uncertainty should be estimated using ISO 11352. Estimation should be based on within-laboratory reproducibility, IRM, and, if available, data from proficiency testings and CRM.

5 Contacts and references

5.1 Contact persons

Anna Willstrand Wranne, SMHI

Johan Håkansson, SMHI

5.2 References

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Chapter 8, p 127-148 in
Grasshoff K, Kremling K and Erhardt M (ed)
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An exact definition of total alkalinity and a procedure for estimation of total alkalinity and total inorganic carbon from titration data
Deep Sea Research Vol 28A p 609-623

Haraldsson C, Andersson L G, Hassellöv M, Hulth S and Olsson K 1997
Rapid, high-precision potentiometric titration of alkalinity in ocean and sediment pore waters
Deep Sea Research Vol 44 p 2031-2044

Millero F. J. and Poisson A 1981
International one-atmosphere equation of state of seawater
Deep Sea Research Vol 28, p 625–629

EN ISO 11352*: Water quality – Estimation of measurement uncertainty based on validation and quality control data

EN ISO/IEC 17025*: General requirements for the competence of testing and calibration laboratories

* For undated references, the latest edition of the referenced document (including any amendments) applies

5.3 Additional literature

Dickson A G, Sabine C L, Christian J R (ed) 2007
Guide to best practices for ocean CO₂ measurements
PICES Special Publication 3
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The influence of dissolved organic matter on the acid–base system of the Baltic Sea
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Modelling organic alkalinity in the Baltic Sea using a Humic-Pitzer approach
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